

Electronic supplementary informations

***N*-Substituted poly(3,6-dithienylcarbazole) derivatives: A new class redox-active electrode materials for high-performance flexible solid-state pseudocapacitors**

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Synthesis of tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2)

3,6-Dibromo-9H-carbazole (1) (0.65 g, 2 mmol), tert-butyl bromoacetate (0.47 g, 2.4 mmol, 1.2 eqv.) and anhydrous cesium carbonate (Cs_2CO_3 , 1.29 g, 4 mmol, 2eqv.) were placed in a glass microwave reaction vessel (30 mL) and a few drops of dry DMF was added. The eventual heterogeneous mixture was heated at 80°C under 100 W single-mode microwave irradiation for 8 min. After cooling room temperature, the slurry mixture was poured out into ice-water (50 mL) and vigorously stirred for 15 min. The aqueous phase was extracted with chloroform (3 x 20 mL), washed with water and brine and dried over anhydrous Na_2SO_4 . The solvent was removed on a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography using dichloromethane as eluent ($R_f = 0.75$) afforded (1.78 mmol, 0.78 g, 89%, mp 133-137°C) as a white solid. FTIR (KBr pellet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3078 (aromatic C-H stretching), 2980, 2911 (aliphatic C-H stretching), 1736 (ester C=O stretching), 1596, 1579 (aromatic C=C stretching), 1473, 1349 (aliphatic C-H bending), 1209 (-C-O- stretching). ^1H NMR δH (400 MHz; CDCl_3 ; Me_4Si) 1.38 (s, 9H, $-\text{CH}_3$), 4.8 (s, 2H, $-\text{CH}_2-$), 7.21 (dd, $J=8.7$ Hz, 2H, Cbz-H), 7.55-7.58 (dd, $J=6.5$ Hz and $J=2$ Hz, 2H, Cbz-H), 8.14 (d, $J=1.6$ Hz, 2H, Cbz-H). MS (EI) m/z 438.9 (M^+ , 2%, $\text{C}_{18}\text{H}_{17}\text{Br}_2\text{NO}_2$, 439.1), 411 (50%), 383 (5%), 338 (100%), 257 (25%), 231 (3%), 207.1 (2%), 178.1 (15%), 151.1 (20%), 125.1 (3%), 89 (10%), 75.2 (10%).

General procedure for synthesis of 3,6-dithienylcarbazole derivatives

The palladium-catalyzed Stille cross-coupling reaction was employed for synthesis of 3,6-dithienylcarbazole derivatives. In a dried 100 mL two-necked round-bottomed flask fitted with a reflux condenser and argon (Ar) inlet, tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2) (0.6 g, 1.36 mmol) and tetrakis(triphenylphosphine) palladium (0) ($\text{Pd}(\text{PPh}_3)_4$, 0.04 g, 0.034 mmol, 0.025 eqv.) were dissolved in dry toluene (20 mL). The light yellow solution was purged with Ar and intensely stirred at room temperature for 15 min. Then, 2-(tributylstannyl)thiophene (1.26 g, 3.4 mmol, 2.5 eqv.) or tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane (1.46 g, 3.4 mmol, 2.5 eqv.) was added via a syringe and the reaction suspension was heated at 110 °C

for 18 h under Ar atmosphere. The dark yellow reaction mixture was cooled to room temperature and toluene was removed on a rotary evaporator under reduced pressure. The oily crude product was subjected to column chromatography using SiO₂ as solid phase and hexane/ethyl acetate mixture as eluent to afford a disered product. The chemical structure of pure monomer was identified by FTIR, ¹H NMR, ¹³C NMR, mass spectrometry techniques and elemental analysis.

Tert-butyl 2-(3,6-di(thien-2-yl)-9H-carbazol-9-yl)acetate (TTBCbz)

This monomer was obtained via Stille cross-coupling reaction of tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2) and 2-(tributylstannyl)thiophene. The crude product was purified by column chromatography using hexane/ethyl acetate (8:1, v/v) as eluent ($R_f = 0.75$) to afford a beige solid product (1.12 mmol, 0.5 g, 83%, mp 144-147°C). FTIR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 3108, 3057 (aromatic C-H stretching), 2981, 2925 (aliphatic C-H stretching), 1734 (ester C=O stretching), 1605, 1577 (aromatic C=C stretching), 1485, 1346 (aliphatic C-H bending), 1220 (-C-O- stretching). ¹H NMR δ H (400 MHz; CDCl₃; Me₄Si) 1.41 (s, 9H, -CH₃), 4.89 (s, 2H, -CH₂), 7.1-7.12 (dd, $J=8.2$ Hz and $J=3.2$ Hz, 2H, Th-H), 7.26-7.28 (dd, $J=6$ Hz and $J=1.2$ Hz, 2H, Th-H), 7.31-7.33 (dd, $J=8.7$ Hz, 2H, Cbz-H), 7.35-7.36 (dd, $J=4.4$ Hz and $J=1.2$ Hz, 2H, Th-H), 7.72-7.75 (dd, $J=6.5$ Hz and $J=2$ Hz, 2H, Cbz-H), 8.33 (d, $J=1.6$ Hz, 2H, Cbz-H). ¹³C NMR δ C (400 MHz; CDCl₃; Me₄Si) 27.9, 45.7, 82.8, 118.1, 122.2, 122.5, 123.5, 123.8, 124.8, 126.6, 128, 140.6, 145.4, 167.2. MS (EI) m/z 445 (M⁺, 40%, C₂₆H₂₃NO₂S₂, 445.6), 417 (15%), 389 (90%), 344 (100%), 299 (5%), 262 (5%), 194 (20%), 172 (20%), 149 (3%), 83 (15%), 56 (20%). Elemental analysis Found: C, 69.76; H, 4.91; N, 3.29. Cald. for C₂₆H₂₃NO₂S₂: C, 70.08; H 5.20; N 3.14%.

Tert-butyl 2-(3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazol-9-yl)acetate (ETBCbz)

This monomer was synthesized via Stille coupling reaction between tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2) and tributyl(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)stannane. The crude product was subjected to column

chromatography using hexane/ethyl acetate (6:1, v/v) as eluent ($R_f = 0.55$). The pure product was obtained as a light brown solid (1.17 mmol, 0.65 g, 86%, mp 132-134°C). FTIR (KBr pellet) $\nu_{\max}/\text{cm}^{-1}$: 3110 (aromatic C-H stretching), 2978, 2851 (aliphatic C-H stretching), 1736 (ester C=O stretching), 1604, 1502 (aromatic C=C stretching), 1483, 1347 (aliphatic C-H bending), 1229 (-C-O- stretching). ^1H NMR δH (400 MHz; CDCl_3 ; Me_4Si) 1.40 (s, 9H, $-\text{CH}_3$), 4.22-4.38 (m, 8H, EDOT- CH_2 -) 4.88 (s, 2H, $-\text{CH}_2$), 6.27 (s, 1H, EDOT-H), 6.29 (s, 1H, EDOT-H), 7.29-7.31 (dd, $J = 8.7$ Hz, 2H, Cbz-H), 7.82-7.84 (dd, $J = 6.5$ Hz and $J = 2$ Hz, 2H, Cbz-H), 8.41 (d, $J = 1.6$ Hz, 2H, Cbz-H). ^{13}C NMR δC (400 MHz; CDCl_3 ; Me_4Si) 27.9, 45.7, 64.5, 64.7, 64.8, 64.9, 82.6, 96.4, 97.5, 108.5, 118.4, 123.5, 124.9, 139.9, 141.2, 167.2. MS (EI) m/z : 561 (M^+ , 2%, $\text{C}_{30}\text{H}_{27}\text{NO}_6\text{S}_2$, 561.6), 501 (40%), 445 (100%), 400 (40%), 365 (20%), 346 (20%), 316 (15%), 262 (25%), 257 (15%), 222 (10%), 185 (25%), 151 (20%), 97 (10%), 57 (25%). Elemental analysis: anal. Found: C, 63.87; H, 4.58; N, 2.32. Cald. for $\text{C}_{30}\text{H}_{27}\text{NO}_6\text{S}_2$: C, 64.15; H, 4.85; N, 2.49%.

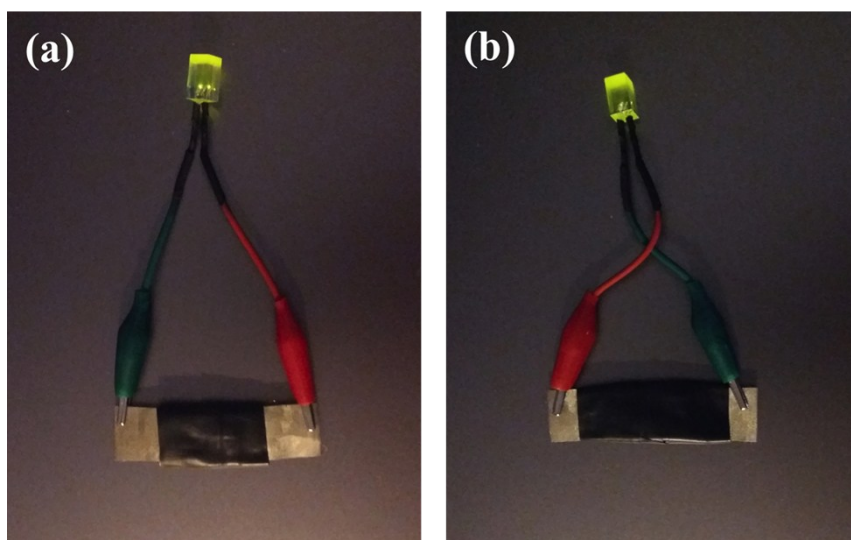


Fig. S1 Two green LEDs powered by (a) Cell I and (b) Cell II flexible solid-state supercapacitor devices.

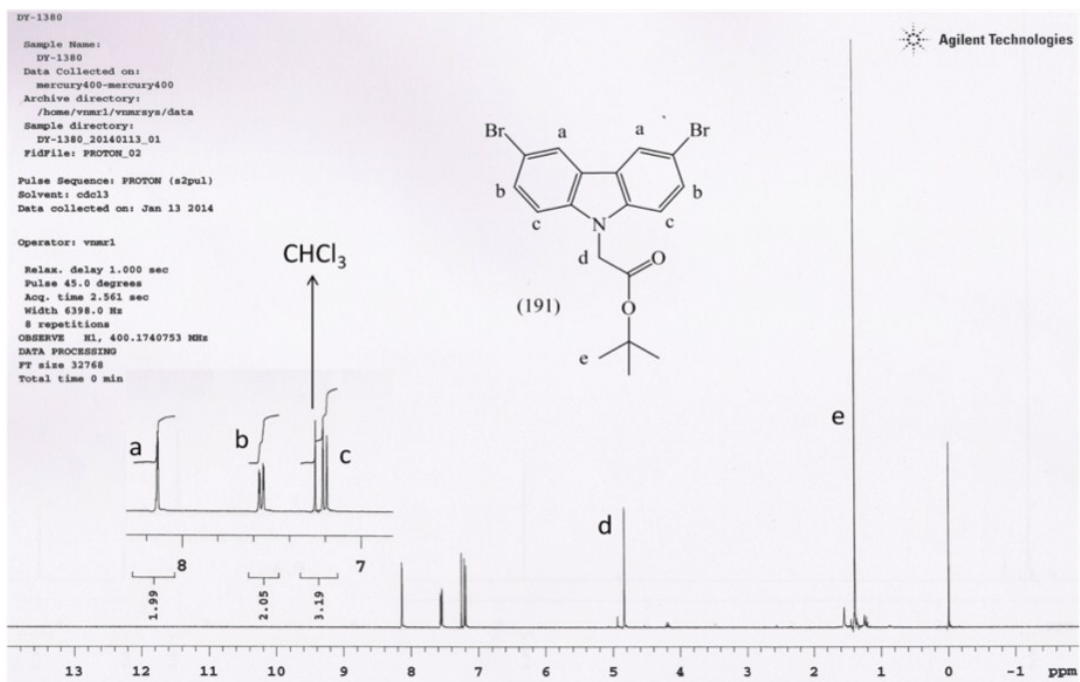


Fig. S2 ¹H NMR spectrum of tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2)

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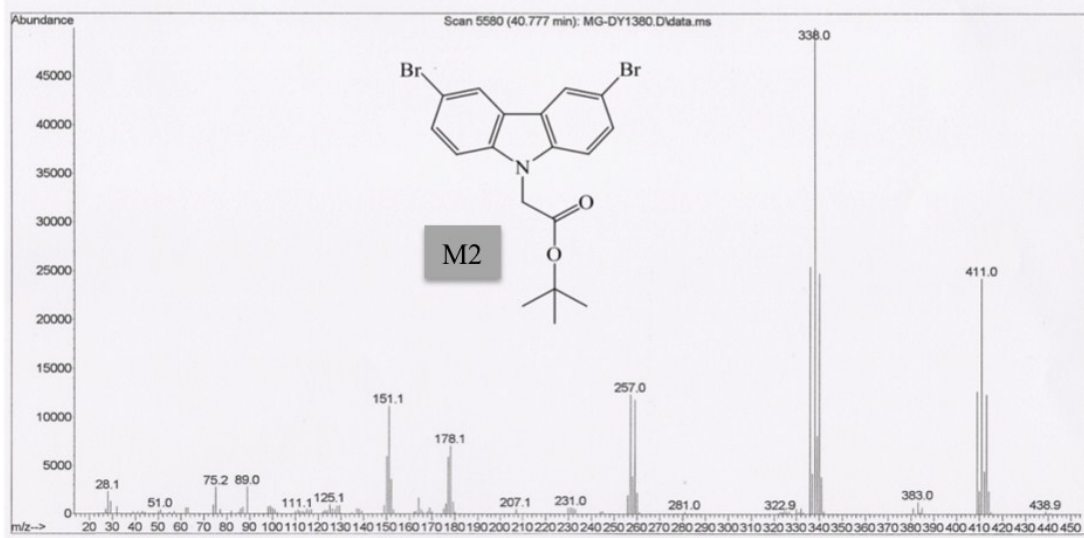


Fig. S3 Mass spectrum of tert-butyl 2-(3,6-dibromo-9H-carbazol-9-yl)acetate (2)

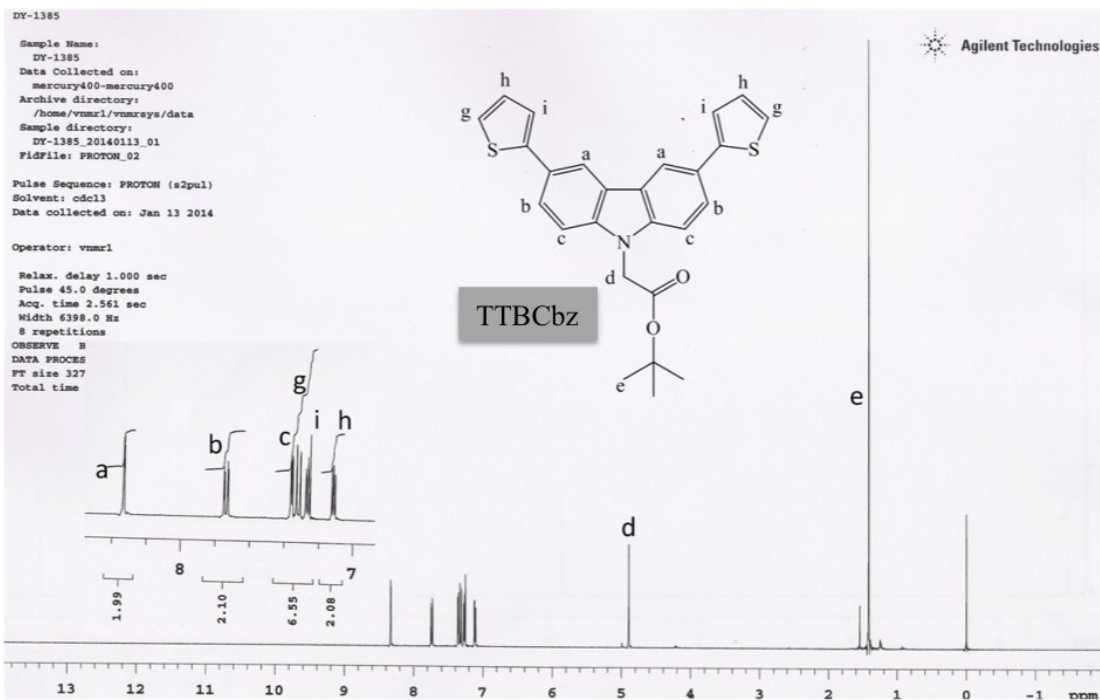


Fig. S4 ^1H NMR spectrum of tert-butyl 2-(3,6-di(thien-2-yl)-9H-carbazol-9-yl)acetate (TTBCbz)

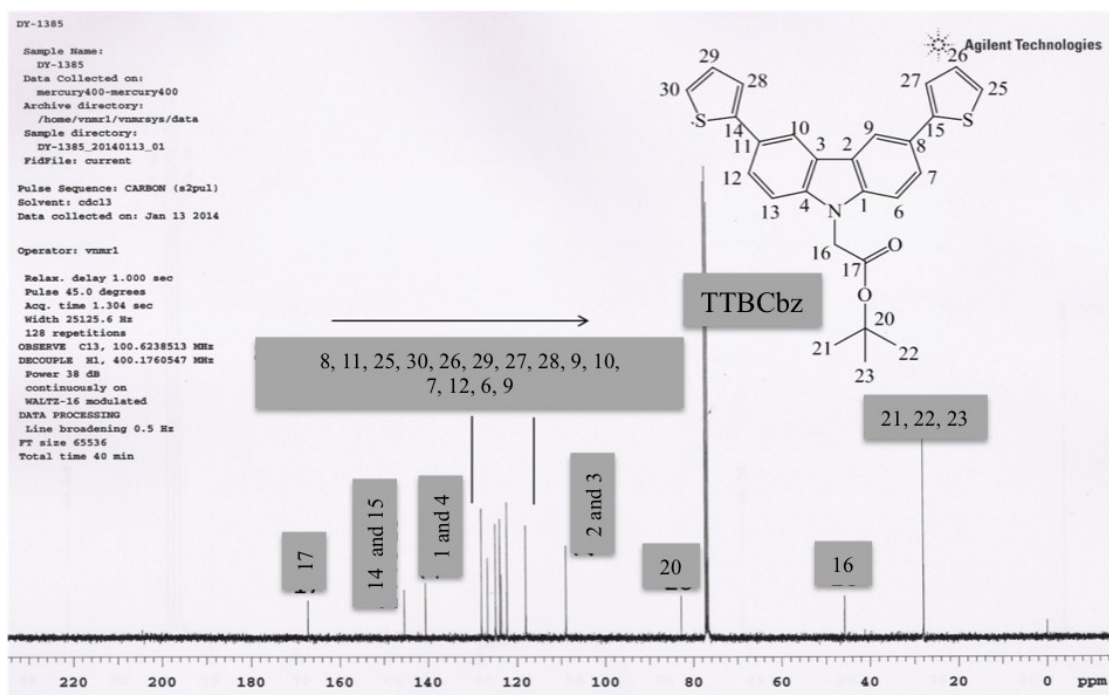


Fig. S5 ^{13}C NMR spectrum of tert-butyl 2-(3,6-di(thien-2-yl)-9H-carbazol-9-yl)acetate (TTBCbz)

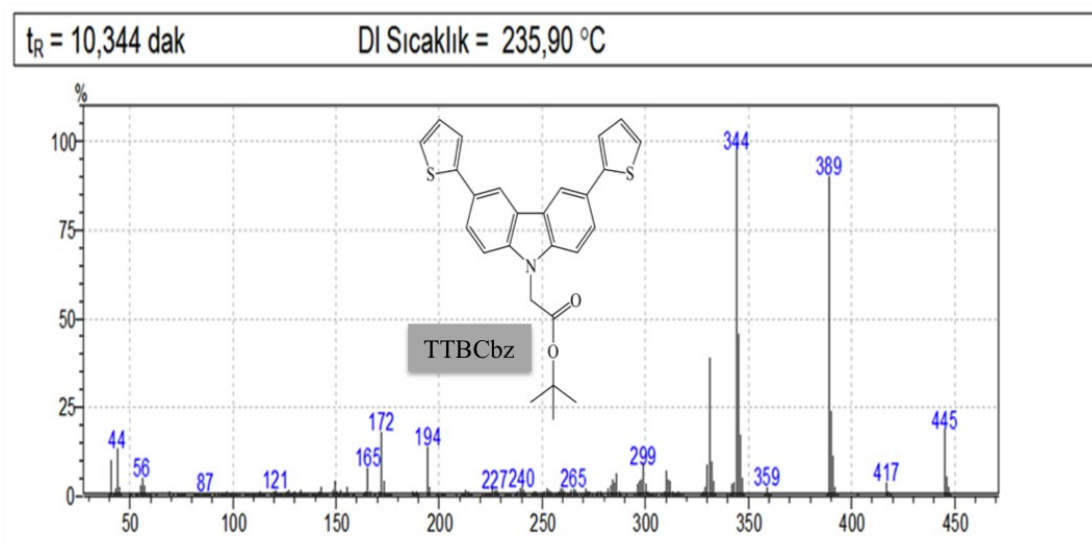


Fig. S6 Mass spectrum of tert-butyl 2-(3,6-di(thien-2-yl)-9H-carbazol-9-yl)acetate (TTBCbz)

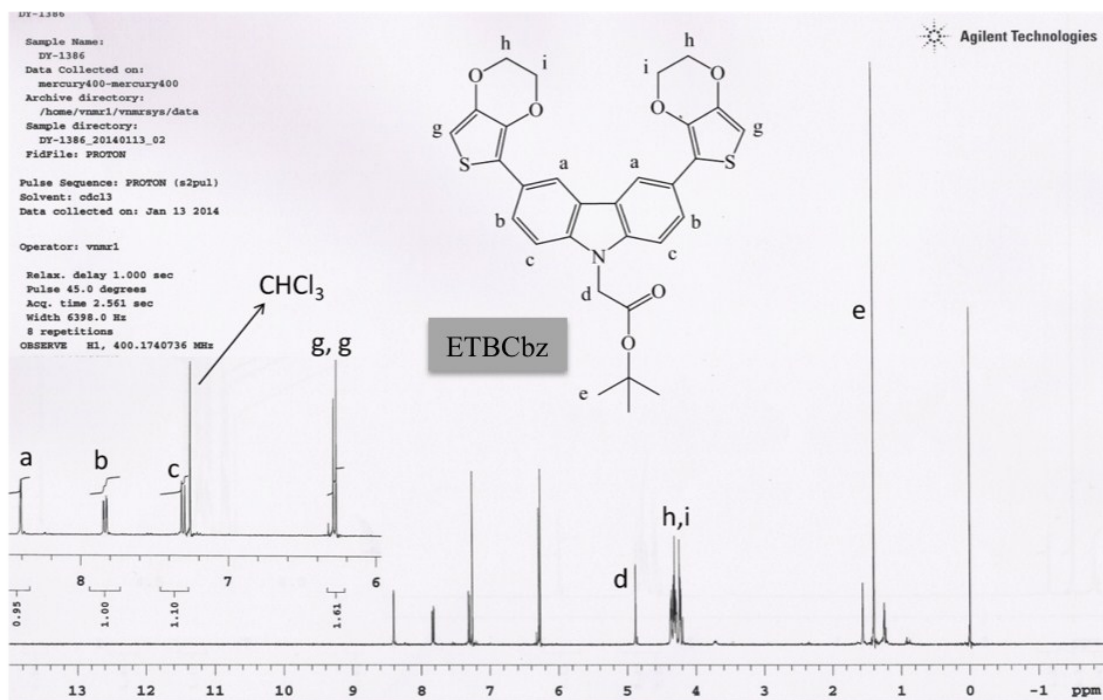


Fig. S7 ¹H NMR spectrum of tert-butyl 2-(3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazol-9-yl)acetate (ETBCbz)

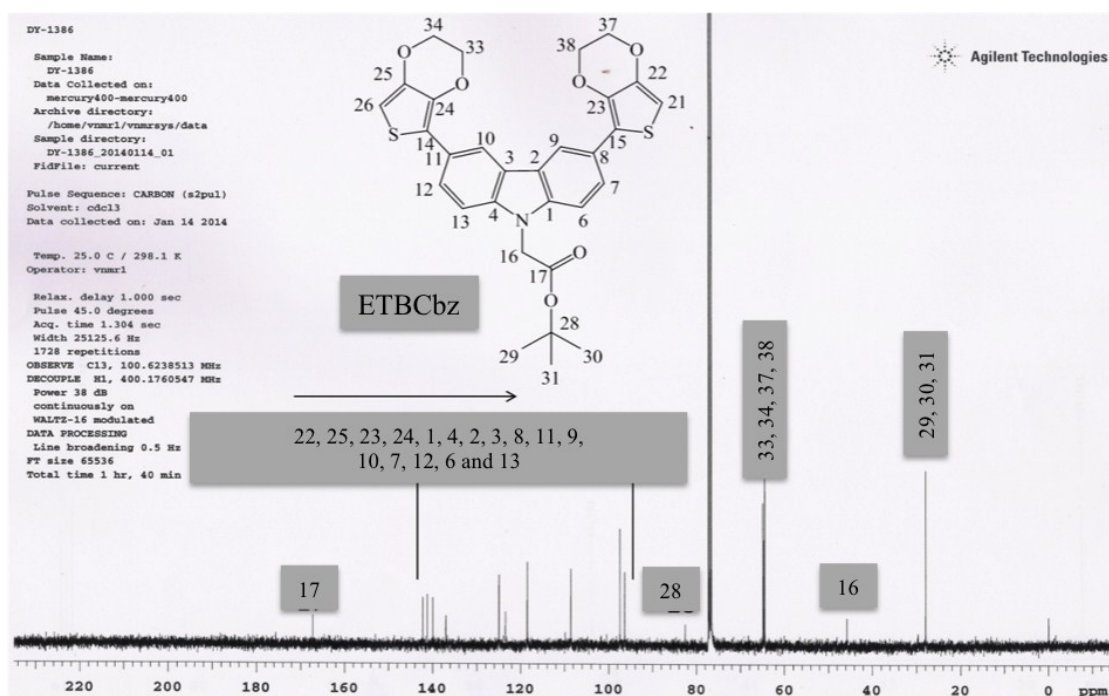


Fig. S8 ¹³C NMR spectrum of tert-butyl 2-(3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazol-9-yl)acetate (ETBCbz)

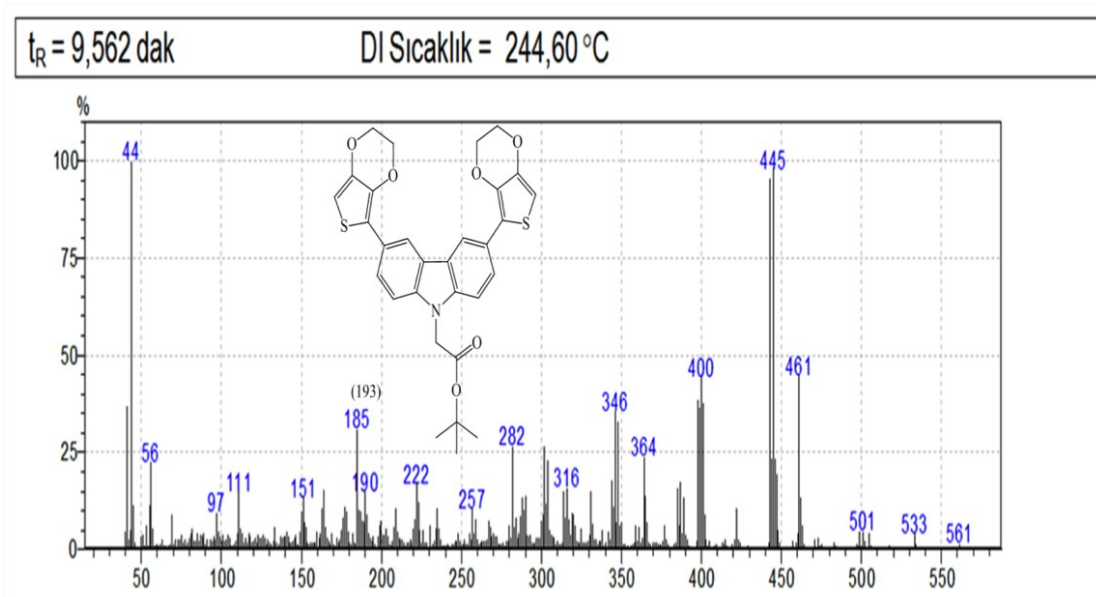


Fig. S9 Mass spectrum of tert-butyl 2-(3,6-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-9H-carbazol-9-yl)acetate (ETBCbz)